



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2499850 C 2006/01/10

(11)(21) **2 499 850**

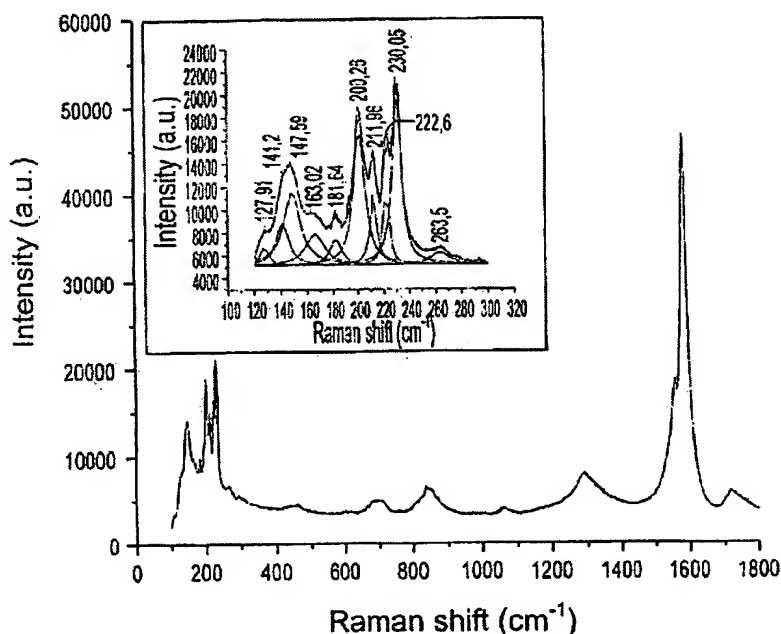
(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2003/05/09
(87) Date publication PCT/PCT Publication Date: 2003/11/20
(45) Date de délivrance/Issue Date: 2006/01/10
(85) Entrée phase nationale/National Entry: 2005/03/24
(86) N° demande PCT/PCT Application No.: CA 2003/000694
(87) N° publication PCT/PCT Publication No.: 2003/095362
(30) Priorité/Priority: 2002/05/09 (2,385,802) CA

(51) Cl.Int.⁷/Int.Cl.⁷ C01B 31/02, B01J 19/08
(72) Inventeurs/Inventors:
SMILJANIC, OLIVIER, CA;
STANSFIELD, BARRY L., CA
(73) Propriétaire/Owner:
INSTITUT NATIONAL DE LA RECHERCHE
SCIENTIFIQUE, CA
(74) Agent: BERESKIN & PARR

(54) Titre : PROCEDE ET DISPOSITIF DE PRODUCTION DE NANOTUBES DE CARBONE A PAROI SIMPLE
(54) Title: METHOD AND APPARATUS FOR PRODUCING SINGLE-WALL CARBON NANOTUBES



(57) Abrégé/Abstract:

The invention relates to a method for producing single-wall carbon nanotubes. The method of the invention comprises the steps of (a) providing a plasma torch having a plasma tube with a plasma-discharging end; (b) feeding an inert gas through the plasma tube to form a primary plasma; (c) contacting a carbon-containing substance and a metal catalyst with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of the metal catalyst; and (d) condensing the atoms or molecules of carbon and the atoms of the metal catalyst to form single-wall carbon nanotubes. Alternatively, steps (b) and (c) can be carried out by feeding an inert gas and an inorganic metal catalyst through the plasma tube to form a primary plasma containing atoms of the inorganic metal catalyst and contacting a carbon-containing substance with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst. An apparatus for carrying out the method according to the invention is also disclosed.

BEST AVAILABLE COPY

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
20 November 2003 (20.11.2003)

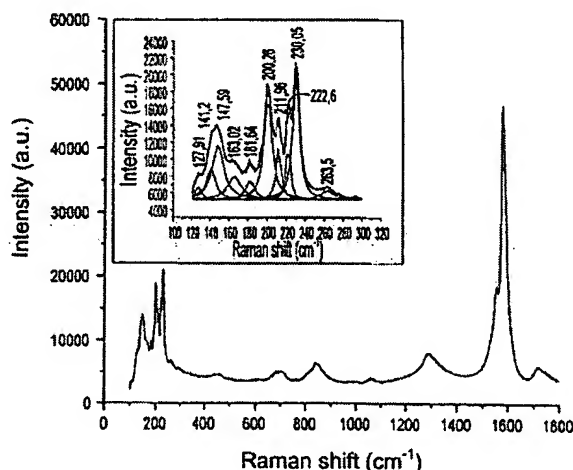
PCT

(10) International Publication Number
WO 2003/095362 A3

- (51) International Patent Classification⁷: C01B 31/02, B01J 19/08 (74) Agents: OGILVY RENAULT et al.; Suite 1600, 1981 McGill College Avenue, Montreal, Québec H3A 2Y3 (CA).
- (21) International Application Number: PCT/CA2003/000694 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 9 May 2003 (09.05.2003) (25) Filing Language: English (26) Publication Language: English
- (30) Priority Data: 2,385,802 9 May 2002 (09.05.2002) CA (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): INSTITUT NATIONAL DE LA RECHERCHE SCIENTIFIQUE [CA/CA]; 1650, boulevard Lionel-Boulet, Varennes, Québec J3X 1S2 (CA).
- (72) Inventors: SMILJANIC, Olivier [CA/CA]; 3590 Ridgewood, Apt. 301, Montreal, Québec H3V 1C2 (CA). STANSFIELD, Barry, L. [CA/CA]; 1140 Montcalm, St. Bruno, Québec J3V 3G8 (CA).
- Published:
— with international search report
- (88) Date of publication of the international search report:
8 April 2004

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR PRODUCING SINGLE-WALL CARBON NANOTUBES



(57) Abstract: The invention relates to a method for producing single-wall carbon nanotubes. The method of the invention comprises the steps of (a) providing a plasma torch having a plasma tube with a plasma-discharging end; (b) feeding an inert gas through the plasma tube to form a primary plasma; (c) contacting a carbon-containing substance and a metal catalyst with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of the metal catalyst; and (d) condensing the atoms or molecules of carbon and the atoms of the metal catalyst to form single-wall carbon nanotubes. Alternatively, steps (b) and (c) can be carried out by feeding an inert gas and an inorganic metal catalyst through the plasma tube to form a primary plasma containing atoms of the inorganic metal catalyst and contacting a carbon-containing substance with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst. An apparatus for carrying out the method according to the invention is also disclosed.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD AND APPARATUS FOR PRODUCING SINGLE-WALL CARBON NANOTUBES

TECHNICAL FIELD

The present invention relates to improvements in the field of
5 carbon nanotube production. More particularly, the invention relates to an
improved method and apparatus for producing single-wall carbon
nanotubes.

BACKGROUND ART

Carbon nanotubes are available either as multi-wall or single-
10 wall nanotubes. Multi-wall carbon nanotubes have exceptional properties
such as excellent electrical and thermal conductivities, and are as strong as
diamond. They have applications in numerous fields such as storage of
hydrogen (C. Liu, Y.Y. Fan, M. Liu, H. T. Cong, H.M. Cheng, M.S.
Dresselhaus, Science 286 (1999), 1127; M.S. Dresselhaus, K.A. Williams,
15 P.C. Eklund, MRS Bull. (1999), 45) or other gases, adsorption heat pumps,
materials reinforcement or nanoelectronics (M. Menon, D. Srivastava, Phy.
Rev. Lett. 79 (1997), 4453). Single-wall carbon nanotubes, on the other
hand, possess properties that are significantly superior to those of multi-
wall nanotubes. However, single-wall carbon nanotubes are available only
20 in small quantities since known methods of production do not produce more
than few grams per day of these nanotubes. For any industrial application
such as storage or material reinforcement, the amount of single-wall carbon
nanotubes produced must be at least a few kilograms per day.

Nowadays, the most popular methods for producing single-
25 wall carbon nanotubes are laser ablation, electric arc and chemical vapor
deposition (CVD). The two first methods are based on the same principal:
local evaporation of a graphite target enriched with a metal catalyst and
subsequent condensation of the vapor to form nanotubes (A.A. Puretzky,

D.B. Geohegan, S.J. Pennycook, Appl. Phys. A 70 (2000), 153). US patent No. 6,183,714 discloses a method of making ropes of single-wall carbon nanotubes using a laser pulse to produce a vapor containing carbon and one or more Group VIII transition metals. US patent No. 5,424,054 discloses a
5 process for producing hollow carbon fibers having wall consisting essentially of a single layer of carbon atoms using an electric arc. The process involves contacting carbon vapor with cobalt vapor under specific conditions, and is thus limited to the use of cobalt vapor.

Although the above methods are relatively efficient for the
10 transformation of carbon into nanotubes, they have inherent drawbacks. The vaporisation of graphite is not energetically advantageous since 717 kJ are required to evaporate one mole of carbon. Therefore, the production of single-wall carbon nanotubes via laser ablation and electric arc consumes a lot of energy for small quantities of nanotubes produced. Moreover, these
15 processes are non-continuous since they must be stopped for renewing the source of carbon once the graphite has been consumed.

In the CVD method as well as in the other two methods described above, the metal catalyst plays a key role in the synthesis of the nanotubes. For example, in the CVD method, the carbon-containing gas is
20 decomposed by the particles of metal catalyst on which the nanotubes form. The CVD method suffers from a major drawback since the encapsulation of the catalyst particles by carbon stops the growth of the nanotubes (R.E. Smalley et al. Chem. Phys. Lett. 296 (1998), 195). In addition, due to the non-selectivity of the method, nanotubes having two, three or multi-walls
25 are obtained at the same time as the single-wall nanotubes.

A promising method for the production of single-wall carbon nanotubes involves the use of a plasma torch for decomposing a mixture of carbon-containing substance and a metal catalyst and then condensing the mixture to obtain single-wall carbon nanotubes. This method has been

recently described by O. Smiljanic, B.L. Stansfield, J.-P. Dodelet, A. Serventi, S. Désilets, in Chem. Phys. Lett. 356 (2002), 189 and showed encouraging results. Such a method, however, has an important drawback since a premature extinction of the plasma torch occurs due to a rapid
5 formation of carbon deposit in the torch. This method is therefore non-continuous and requires removal of the carbon deposit. Thus, large quantities of single-wall carbon nanotubes cannot be produced.

DISCLOSURE OF THE INVENTION

It is therefore an object of the present invention to overcome
10 the above drawbacks and to provide a method and apparatus for the continuous production of single-wall carbon nanotubes in large quantities.

According to a first aspect of the invention, there is provided a method for producing single-wall carbon nanotubes, comprising the steps of:

- 15 a) providing a plasma torch having a plasma tube with a plasma-discharging end;
- b) feeding an inert gas through the plasma tube to form a primary plasma;
- c) contacting a carbon-containing substance and a metal
20 catalyst with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of metal catalyst; and
- d) condensing the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes.

25 According to a second aspect of the invention, there is provided a method for producing single-wall carbon nanotubes, comprising the steps of:

- a) providing a plasma torch having a plasma tube with a plasma-discharging end;

b) feeding an inert gas and an inorganic metal catalyst through the plasma tube to form a primary plasma containing the atoms of metal catalyst;

c) contacting a carbon-containing substance with the primary
5 plasma at the plasma-discharging end of said plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst; and

d) condensing the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes.

10 According to a third aspect of the invention, there is provided an apparatus for producing single-wall carbon nanotubes, which comprises:

a plasma torch having a plasma tube for receiving an inert gas so as to form a primary plasma, the plasma tube having a plasma-discharging end;

15 feed means for directing a carbon-containing substance and a metal catalyst towards the primary plasma so that the carbon-containing substance and the metal catalyst contact the primary plasma at the plasma-discharging end of the plasma tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of the metal
20 catalyst; and

condensing means for condensing the atoms or molecules of carbon and the atoms of the metal catalyst to form single-wall carbon nanotubes.

25 According to a fourth aspect of the invention, there is provided an apparatus for producing single-wall carbon nanotubes, which comprises:

a plasma torch having a plasma tube for receiving an inert gas and an inorganic metal catalyst so as to form a primary plasma containing

atoms of the metal catalyst, the plasma tube having a plasma-discharging end;

5 feed means for directing a carbon-containing substance towards the primary plasma so that the carbon-containing substance contacts the primary plasma at the plasma-discharging end of the plasma tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of the metal catalyst; and

10 condensing means for condensing the atoms or molecules of carbon and the atoms of the metal catalyst to form single-wall carbon nanotubes.

Applicant has found quite surprisingly that by feeding the carbon-containing substance separately from the inert gas used to generate the primary plasma so that the carbon-containing substance contacts the primary plasma at the plasma-discharging end of the plasma tube to form
15 the aforesaid secondary plasma, there is no undesirable formation of carbon deposit adjacent the plasma-discharging end of the plasma tube. Thus, no premature extinction of the plasma torch.

The term "carbon-containing substance" as used herein refers to a substance which contains carbon atoms. Preferably, such a substance
20 does not contain nitrogen atoms. The carbon-containing substance can be a solid, a liquid or a gas.

The expression "organometallic complex" as used herein refers to a compound in which there is a bonding interaction (ionic or covalent, localized or delocalized) between one or more carbon atoms of an
25 organic group or molecule with a main group, transition, lanthanide, or actinide metal atom or atoms.

The expression "rapid condensation" as used herein refers to a condensation which occurs at a rate of at least 10^5 K / second.

MODES FOR CARRYING OUT THE INVENTION

In the method according to the first aspect of the invention, step (c) can be carried out by separately directing the carbon-containing substance and the metal catalyst towards the primary plasma. The carbon-containing substance can be in admixture with a carrier gas. Preferably, the carbon-containing substance is in liquid or gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma. The carbon-containing substance in liquid or gaseous phase is preferably in admixture with a carrier gas. It is also possible to use a carbon-containing substance in solid phase, in admixture with a carrier gas; such a mixture preferably flows along a helical path prior to contacting the primary plasma. The metal catalyst can also be in admixture with a carrier gas. When use is made of a metal catalyst in liquid or gaseous phase, such a metal catalyst preferably flows along a helical path prior to contacting the primary plasma. The metal catalyst in liquid or gaseous phase is preferably in admixture with a carrier gas. It is also possible to use a metal catalyst in solid phase, in admixture with a carrier gas; such a mixture preferably flows along a helical path prior to contacting the primary plasma.

Step (c) of the method according to the first aspect of the invention can also be carried out by directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma. The latter mixture can be in admixture with a carrier gas. Preferably, the carbon-containing substance and the metal catalyst are in liquid or gaseous phase and the latter two flow along a helical path prior to contacting the primary plasma. The carbon-containing substance and the metal catalyst in liquid or gaseous phase are preferably in admixture with a carrier gas. It is also possible to use the carbon-containing substance and the metal catalyst

in solid phase, in admixture with a carrier gas; such a mixture preferably flows along a helical path prior to contacting the primary plasma.

The metal catalyst used in the method according to the first aspect of the invention is preferably an organometallic complex. It is also possible to use, as a metal catalyst, an inorganic metal complex or an inorganic metal catalyst comprising at least one metal in metallic form. Examples of suitable metal catalyst include those comprising at least one metal selected from the group consisting of Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Ce, Mn, Li, Pr, Nd, Tb, Dy, Ho, Er, Lu and Gd. The metal is preferably iron.

The metal catalyst can also comprise cobalt and at least one metal selected from the group consisting of Ni, Fe, Y, Pt, Mo, Cu, Pb and Bi. Alternatively, the metal catalyst can comprise nickel and at least one metal selected from the group consisting of Fe, Y, Lu, Pt, B, Ce, Mg, Cu and Ti.

Ferrocene, iron (II) phthalocyanine, iron in metallic form, iron pentacarbonyl and mixtures thereof can be used as suitable metal catalyst. Ferrocene is preferred.

In the method according to the first aspect of the invention, it is possible to use the inert gas in admixture with an inorganic metal catalyst which may be the same or different than the one used in step (c).

In the method according to the second aspect of the invention, step (c) can be carried out by directing the carbon-containing substance towards the primary plasma. The carbon-containing substance can be in admixture with a carrier gas. Preferably, the carbon-containing substance is in liquid or gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma. The carbon-containing substance in liquid or gaseous phase is preferably in admixture with a carrier gas. It is also possible to use a

carbon-containing substance in solid phase, in admixture with a carrier gas; such a mixture preferably flows along a helical path prior to contacting the primary plasma.

The inorganic metal catalyst used in the method according to the second aspect of the invention can be an inorganic metal complex or at least one metal in metallic form. Preferably, the inorganic metal catalyst comprises at least one metal selected from the group consisting of Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Ce, Mn, Li, Pr, Nd, Tb, Dy, Ho, Er, Lu and Gd. The metal is preferably iron. The inorganic metal catalyst can also comprise cobalt and at least one metal selected from the group consisting of Ni, Fe, Y, Pt, Mo, Cu, Pb and Bi. Alternatively, the inorganic metal catalyst can comprise nickel and at least one metal selected from the group consisting of Fe, Y, Lu, Pt, B, Ce, Mg, Cu and Ti.

The carbon-containing substance used in the method according to the first or the second aspect of the invention can be a carbon-containing gas, a carbon-containing liquid or a carbon-containing solid. It is also possible to use a mixture of a carbon-containing gas and a carbon-containing liquid, a mixture of a carbon-containing gas and a carbon-containing solid, a mixture of a carbon-containing liquid and a carbon-containing solid or a mixture of a carbon-containing gas, a carbon-containing liquid and a carbon-containing solid. Preferably, the carbon-containing gas is a C₁-C₄ hydrocarbon such as methane, ethane, ethylene, acetylene, propane, propene, cyclopropane, allene, propyne, butane, 2-methylpropane, 1-butene, 2-butene, 2-methylpropene, cyclobutane, methylcyclopropane, 1-butyne, 2-butyne, cyclobutene, 1,2-butadiene, 1,3-butadiene or 1-buten-3-yne or a mixture thereof. When commercial acetylene is used, care should be taken to filter such a gas in order to remove impurities. The carbon-containing liquid is preferably a C₅-C₁₀ hydrocarbon. Alternatively, the carbon-containing liquid can be selected

from the group consisting of pentane, hexane, cyclohexane, heptane, benzene, toluene, xylene or styrene or mixtures thereof. The carbon-containing solid can be graphite, carbon black, norbornylene, naphthalene, anthracene, phenanthrene, polyethylene, polypropylene, or polystyrene or mixtures thereof. Graphite is preferred. More preferably, the graphite is in the form of a nano-powder.

The inert gas used in the method according to the first or second aspect of the invention can be helium, argon or a mixture thereof. Argon is preferred. A further inert gas can be injected in the plasma torch and directed towards the primary and secondary plasmas. A cooling inert gas is preferably injected downstream of the secondary plasma; the cooling inert gas can be helium, argon or a mixture thereof. The cooling inert gas assists in providing a temperature gradient. The aforementioned carrier gas can be helium, argon, hydrogen or hydrogen sulfide or a mixture thereof. Argon is preferably used as carrier gas.

According to a preferred embodiment, the metal catalyst and the carbon-containing substance are used in an atomic ratio metal atoms / carbon atoms of about 0.01 to about 0.06. More preferably, the atomic ratio metal atoms / carbon atoms is about 0.02.

Step (d) of the method according to the first or second aspect of the invention is preferably carried out to provide a temperature gradient permitting rapid condensation of the atoms or molecules of carbon and the atoms of metal catalyst. Preferably, the temperature gradient is provided by directing the atoms or molecules of carbon and the atoms of metal catalyst through an oven disposed downstream of the plasma tube in spaced relation thereto, the oven being heated at a predetermined temperature. The predetermined temperature can be comprised between 500 and 1800 °C and preferably between 800 and 950 °C. A temperature of about 900 °C is

preferred. Such a temperature of about 900.°C is also particularly preferred when the metal catalyst comprises iron. The single-wall carbon nanotubes produced can be collected in a trap such as an electrostatic trap.

In the apparatus according to the third aspect of the invention,
5 the feed means preferably comprise a first conduit for directing the carbon-containing substance towards the primary plasma and a second conduit for directing the metal catalyst towards the primary plasma. Preferably, the first and second conduits each have a discharge end disposed adjacent the plasma-discharging end of the plasma tube. Alternatively, the feed means
10 can comprise a single conduit for directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma. In such a case, the single conduit preferably has a discharge end disposed adjacent the plasma-discharging end of the plasma tube. In a particularly preferred embodiment, the single conduit is disposed inside the plasma tube
15 and extends substantially coaxially thereof.

In the apparatus according to the fourth aspect of the invention, the feed means preferably comprises a single conduit for directing the carbon-containing substance towards the primary plasma. Preferably, the conduit has a discharge end disposed adjacent the plasma-
20 discharging end of the plasma tube. In a particularly preferred embodiment, the conduit is disposed inside the plasma tube and extends substantially coaxially thereof.

In the apparatus according to the third or fourth aspect of the invention, the condensing means preferably comprise an oven disposed
25 downstream of the plasma tube in spaced relation thereto, and a heat source for heating the oven to provide a temperature gradient permitting rapid condensation of the atoms or molecules of carbon and the atoms of metal catalyst. Preferably, a heat-resistant tubular member having a plasma-receiving end extends through the oven with the plasma-receiving end

disposed upstream of the plasma-discharging end of the plasma tube. Injection means are provided for injecting a cooling inert gas into the tubular member, downstream of the secondary plasma; the cooling inert gas assists in providing the temperature gradient. The heat-resistant tubular member can be made of quartz or boron nitride. The apparatus can be provided with a trap for collecting single-wall carbon nanotubes produced. Preferably, the trap is an electrostatic trap. The apparatus can also be provided with a cooling system disposed about the plasma tube and extends substantially coaxially thereof. Preferably, the apparatus comprises a Faraday shield made of a conductive material for preventing emission of electromagnetic radiations outside of the apparatus.

Where the apparatus according to the third or fourth aspect of the invention has the aforementioned conduit disposed inside the plasma tube and extending substantially coaxially thereof, the apparatus preferably includes another heat-resistant tubular member disposed about the plasma tube and extending substantially coaxially thereof, and means for injecting a further inert gas between the plasma tube and the tubular member to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end of the plasma tube. The latter heat-resistant tubular member can also be made of quartz or boron nitride.

DESCRIPTION OF DRAWINGS

Further features and advantages of the invention will become more readily apparent from the following description of preferred embodiments as illustrated by way of examples in the appended drawings wherein:

Fig. 1 is a schematic, sectional elevation view of an apparatus for producing single-wall carbon nanotubes, according to a first preferred embodiment of the invention;

Fig. 2 is a schematic, sectional elevation view of an apparatus for producing single-wall carbon nanotubes, according to a second preferred embodiment of the invention;

Fig. 3 is a schematic, sectional elevation view of an apparatus
5 for producing single-wall carbon nanotubes, according to a third preferred embodiment of the invention;

Fig. 4 is a schematic, sectional elevation view of an injecting device according to a fourth preferred embodiment of the invention;

Fig. 5 is a SEM (Scanning Electron Microscope) picture of a
10 crude sample of single-wall carbon nanotubes;

Fig. 6 is another SEM picture of the sample shown in Fig. 5;

Fig. 7 is a TEM (Transmission Electron Microscope) picture of the sample shown in Fig. 5;

Fig. 8 is another TEM picture of the sample shown in Fig. 5;

Fig. 9 is the graph of a Raman spectroscopy measurement
15 performed on the sample shown in Fig. 5 using a 514 nm laser; and

Fig. 10 is the graph of another Raman spectroscopy measurement performed on the sample shown in Fig. 5 using a 782 nm laser.

20 Referring first to Fig. 1, there is shown an apparatus 10 for producing single-wall carbon nanotubes, which comprises a plasma torch 12 having a plasma tube 14 with a plasma-discharging end 16, and an oven 18 disposed downstream of the plasma tube 14 in spaced relation thereto. The plasma tube 14 is adapted to receive an inert gas for activation by
25 electromagnetic radiation generated from a source (not shown) so as to form a primary plasma 20. The electromagnetic radiations are propagated on the plasma tube 14 so as to maintain the primary plasma 20. The primary plasma 20 comprises ionized atoms of the inert gas. A feed conduit 22 having a discharge end 24 is arranged inside the plasma tube 14 and extends

substantially coaxially thereof. The discharge end 24 of the feed conduit 22 is disposed adjacent the plasma discharging end 16 of the plasma tube 14. The feed conduit 22 serves to direct a carbon-containing substance, such as a carbon-containing gas, and a metal catalyst towards the primary plasma 20 so that the carbon-containing substance and the metal catalyst contact the primary plasma 20 at the plasma-discharging end 16 of the plasma tube 14, whereby to form a secondary plasma 26 containing atoms or molecules of carbon and the atoms of metal catalyst. The carbon-containing gas is preferably ethylene or methane.

10 The oven 18 serves to condense the atoms or molecules of carbon and atoms of metal catalyst to form single-wall carbon nanotubes 28. A heat source 30 is provided for heating the oven 18 to generate a temperature gradient permitting rapid condensation of the atoms or molecules of carbon and the atoms of metal catalyst. A heat-resistant tubular member 32 having a plasma-receiving end 34 extends through the oven 18, the plasma-receiving end 34 being disposed upstream of the plasma-discharging end 16 of the plasma tube 14. An electrostatic trap 35 comprising a filter 36 and a rod 37 is extending downstream of oven 18. The deposit of single-wall carbon nanotubes 28 occurs on the heat-resistant member 32 upstream and downstream of the oven 18, as well as inside of the trap 35. The filter 36 traps some of the fine particles (not shown) generated during the formation of single-wall carbon nanotubes 28 and reduces the emission of fine particles outside of the apparatus. The electrostatic trap 35 permits a more efficient recovery of the single-wall nanotubes produced by the apparatus 10. The apparatus further includes a gas injector 38 for injecting a cooling inert gas into the tubular member 32, downstream of the secondary plasma 26. The cooling inert gas assists in providing the temperature gradient. Another heat-resistant tubular member 40 is disposed about the plasma tube 14 and extends substantially coaxially

thereof, the tubular member 40 being fixed to the tubular member 32 and supporting same. Another gas injector 42 is provided for injecting a further inert gas between the plasma tube 14 and the tubular member 40 to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end 16 of the plasma tube 14. The plasma tube 14 is also provided with a cooling system (not shown), which preferably uses water. The apparatus 10 further comprises a Faraday shield (not shown) made of a conductive material, preferably aluminium.

The inert gas flows through the plasma tube 14 along a helical path represented by the arrow 44. Similarly, the carbon-containing gas and the metal catalyst, optionally in admixture with a carrier gas, flow through the feed conduit 22 along a helical path represented by the arrow 46. The metal catalyst which is fed through the conduit 22 can be either an organometallic complex such as ferrocene, or an inorganic metal catalyst such as iron in metallic form. Instead of feeding the metal catalyst through the conduit 22, it is possible to feed only the carbon-containing gas through the conduit 22 and to feed the metal catalyst in admixture with the inert gas through the plasma tube 14. In such a case, the metal catalyst must be an inorganic metal catalyst to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end 16 of the plasma tube 14. It is also possible to feed the inert gas and an inorganic metal catalyst through the plasma tube 14 and to feed the carbon-containing gas in admixture with an organometallic complex or an inorganic metal catalyst through the conduit 22.

Figure 2 illustrates another apparatus 48 for producing single-wall carbon nanotubes, which comprises a plasma torch 50 having a plasma tube 52 with a plasma-discharging end 54, and an oven 56 disposed downstream of the plasma tube 52 in spaced relation thereto. The plasma tube 52 is adapted to receive an inert gas for activation by electromagnetic

radiation generated from a source (not shown) so as to form a primary plasma 58. A feed conduit 60 having a discharge end 62 disposed adjacent the plasma-discharging end 54 of the plasma tube 52 is provided for directing a carbon-containing substance, such as a carbon-containing gas, and a metal catalyst towards the primary plasma 58. The carbon-containing substance and the metal catalyst discharged from the feed conduit 60 contact the primary plasma 58 at the plasma-discharging end 54 of the plasma tube 52, thereby forming a secondary plasma 64 containing atoms or molecules of carbon and the atoms of metal catalyst. The carbon-containing gas is preferably ethylene or methane. Although only one feed conduit 60 is shown in Fig. 2, it is possible to have a plurality of such conduits disposed symmetrically about the plasma tube 52. The plasma tube 52 is also provided with a cooling system (not shown), which preferably uses water. The apparatus 48 further comprises a Faraday shield (not shown) made of a conductive material, preferably aluminium.

The oven 56 serves to condense the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes 66. A heat source 68 is provided for heating the oven 56 to generate a temperature gradient permitting rapid condensation of the atoms or molecules of carbon and the atoms of metal catalyst. A heat-resistant tubular member 70 having a plasma-receiving end 72 extends through the oven 56, the plasma-receiving end 72 being disposed upstream of the plasma-discharging end 54 of the plasma tube 52. The apparatus further includes a gas injector 74 for injecting a cooling inert gas into the tubular member 70, downstream of the secondary plasma 64. The cooling inert gas assists in providing the temperature gradient. The deposit of single-wall carbon nanotubes 66 occurs on the heat-resistant tubular member 70 upstream and downstream of the oven 56.

The inert gas flows through the plasma tube 52 along a helical path represented by the arrow 76. Similarly, the carbon-containing gas and the metal catalyst, optionally in admixture with a carrier gas, flow through the conduit 60 along a helical path represented by the arrow 78. The metal catalyst which is fed through the conduit 60 can be either an organometallic complex such as ferrocene, or an inorganic metal catalyst such as iron. Instead of feeding the metal catalyst through the conduit 60, it is possible to feed only the carbon-containing gas through the conduit 60 and to feed the metal catalyst in admixture with the inert gas through the plasma tube 52. In such a case, the metal catalyst must be an inorganic metal catalyst to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end 54 of the plasma tube 52. It is also possible to feed the inert gas and an inorganic metal catalyst through the plasma tube 52 and to feed the carbon-containing gas in admixture with an organometallic complex or an inorganic metal catalyst through the conduit 60. Optionally, the apparatus 48 can be provided with the electrostatic trap 35 illustrated in Fig. 1.

The apparatus 48' illustrated in Fig. 3 is similar to the apparatus 48 shown in Fig. 2, with the exception that an additional feed conduit 60' is provided, the feed conduits 60 and 60' being arranged on either side of the plasma tube 52. The conduit 60' has a discharge end 62' disposed adjacent the plasma-discharging end 54 of the plasma tube 52 and serves the same purpose as the feed conduit 60. The carbon-containing gas and the metal catalyst, optionally in admixture with a carrier gas, flow through the conduit 60' along a helical path represented by the arrow 78'. Although two feed conduits 60 and 60' are shown in Fig. 3, it is possible to have a plurality of such conduits disposed symmetrically about the plasma tube 52. Instead of feeding the metal catalyst through the conduits 60 and 60', it is possible to feed only the carbon-containing gas through the

conduits 60 and 60' and to feed the metal catalyst in admixture with the inert gas through the plasma tube 52. In such a case, the metal catalyst must be an inorganic metal catalyst to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end 54 of the plasma tube 52. It is also possible to feed the inert gas and an inorganic metal catalyst through the plasma tube 52 and to feed the carbon-containing gas in admixture with an organometallic complex or an inorganic metal catalyst through the conduits 60 and 60'. The plasma tube 52 is also provided with a cooling system (not shown), which preferably uses water. The apparatus 48' further comprises a Faraday shield (not shown) made of a conductive material, preferably aluminium. Optionally, the apparatus 48' can be provided with the electrostatic trap 35 illustrated in Fig. 1.

Fig. 4 illustrates an injecting device 80 comprising a reservoir 82 adapted to receive an oil 84, and a reservoir 86 having filters 88. The reservoir 86 is forming a chamber 89 for receiving a metal catalyst 90, preferably ferrocene. The reservoir 86 has an inlet 92 and an outlet 94, which are in fluid flow communication with conduits 96 having an inlet 98 and an outlet 100.

The chamber 89 of the reservoir 86 is provided with a metal catalyst 90 and the catalyst 90 is heated by the hot oil 84 so as to evaporate the metal catalyst 90. A mixture of a carbon-containing gas and a carrier gas (not shown) or a carbon-containing gas is injected at the inlet 98 so as to flow into conduits 96 thereby passing through the reservoir 86 and carrying the evaporated metal catalyst 90 at the outlet 100, which is connected to the apparatus 10, 48 or 48'. The filters 88 prevent solid particles of the metal catalyst 90 from being carried out into said conduits 96.

The following non-limiting example further illustrates the invention.

EXAMPLE

The production or synthesis of single-wall carbon nanotubes has been performed by using a plasma torch as illustrated in Fig. 1. The following experiment has been carried out by the inventors by providing the plasma torch with a cooling system and a Faraday shield. The cooling system prevents the plasma torch from over-heating and being damaged. The Faraday shield comprising a conductive material, preferably aluminium, prevents the electromagnetic radiations from escaping from said apparatus, thereby protecting users of the plasma torch. All the parameters related to the plasma torch are controlled by a computer using the LABVIEW[®] software. The parameters can also be manually controlled. The inert gas used for generating the primary plasma was argon, the metal catalyst was ferrocene, the carbon-containing gas was ethylene and the cooling gas was helium. Helium was also injected toward the plasma discharging end so as to prevent carbon deposit. The injecting device illustrated in Fig. 4 was used for injecting the ferrocene. Ferrocene was heated to 100 °C and the conduits were heated to 250 °C so as to prevent condensation of ferrocene in the conduit disposed downstream of the reservoir containing the latter metal catalyst. The argon flow varied from 1000 to 3000 sccm (standard cubic centimetres per minute). The helium flows were both stabilized at about 3250 sccm, and the ethylene flow varied between 50 and 100 sccm. The temperature of the oven was kept at 900°C and measured with a pyrometer. The power of the source generating the electromagnetic radiations (microwaves) was 1000 W and the reflected power was about 200 W. The rod of the electrostatic trap was maintained at a tension of -1000 V. The heat-resistant tubular members were made of quartz. The plasma tube was made of brass. The feed conduit, on the other hand, was made of stainless steel. The metal catalyst (ferrocene) and the carbon-containing substance (ethylene) were used in an atomic ratio metal

atoms / carbon atoms of 0.02. The software controlled the flow of the carrier gas, argon, so as to maintain the atomic ratio at such a value. The experiment was carried out at atmospheric pressure under inert conditions (helium and argon).

5 The synthesis of single-wall carbon nanotubes was performed for a period of 20 minutes using the above-mentioned experimental conditions. During this period of time, 500 mg of the desired single-wall carbon nanotubes were produced. The purity of the nanotubes thus obtained was about 20 %.

10 The crude sample obtained in the above example was characterized by SEM; the results are illustrated in Figs. 5 and 6. As it is apparent from Figs. 5 and 6, single-wall carbon nanotubes were produced. The sample was also characterized by TEM; the results are illustrated in Figs. 7 and 8. These two figures show that the growth of the single-wall
15 nanotubes is initiated by metal catalyst particles of about 5 nm (indicated by the arrows). The rope-like structure shown in Figs. 7 and 8 is very common for single-wall nanotubes. The purity of the sample was estimated by comparing the surface occupied by the single-wall carbon nanotubes with the amorphous carbon residues in Figs. 7 and 8.

20 In order to determine the diameter of the single-wall nanotubes produced according to the above example, two Raman spectroscopy measurements were performed. In the first experiment, a 514 nm laser was used (Fig. 9) whereas, in the second experiment, a 782 nm laser was used (Fig. 10). In Fig. 9, the peaks at 149.10, 171.90,
25 184.22, 217.75 and 284.79 cm^{-1} correspond to single-wall carbon nanotubes having diameters of 1.50, 1.30, 1.22, 1.03 and 0.80 nm, respectively.

In Fig. 10, the peaks at 127.91, 141.20, 147.59, 163.02, 181.64, 200.26, 211.96, 222.60, 230.05 and 263.57 cm^{-1} correspond to

single-wall carbon nanotubes having diameters of 1.75, 1.60, 1.52, 1.37, 1.23, 1.12, 1.06, 1.00, 0.97 and 0.85 nm, respectively.

The above data indicate that in the method according to the example, as opposed to the methods comprising vaporization of graphite, a
5 plurality of single-wall nanotube chiralities was obtained.

It should be noted that by using the method and apparatus of the invention, the production of single-wall carbon nanotubes can be performed for a period of several hours since the deposit of carbon at the plasma-discharging end, leading to the premature extinction of the plasma
10 torch, is avoided.

CLAIMS:

1. A method for producing single-wall carbon nanotubes, comprising the steps of:
 - a) providing a plasma torch having a plasma tube with a
5 plasma-discharging end;
 - b) feeding an inert gas through said plasma tube to form a primary plasma;
 - c) contacting a carbon-containing substance and a metal catalyst with said primary plasma at the plasma-discharging end of said plasma
10 tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of said metal catalyst; and
 - d) condensing the atoms or molecules of carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.
2. The method of claim 1, wherein step (c) is carried out by
15 separately directing the carbon-containing substance and the metal catalyst towards the primary plasma.
3. The method of claim 1 or 2, wherein the carbon-containing substance is in liquid or gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the
20 primary plasma.
4. The method of any one of claims 1 to 3, wherein the carbon-containing substance is in gaseous phase and the carbon-containing substance in gaseous phase is in admixture with a carrier gas.

5. The method of any one of claims 1 to 3, wherein the carbon-containing substance is in liquid phase and the carbon-containing substance in liquid phase is in admixture with a carrier gas.
6. The method of claim 1 or 2, wherein the carbon-containing substance is in solid phase and the carbon-containing substance in solid phase is in admixture with a carrier gas, and wherein the mixture of the carbon-containing substance in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.
7. The method of any one of claims 1 to 6, wherein the metal catalyst is in liquid or gaseous phase and the metal catalyst in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma.
8. The method of any one of claims 1 to 7, wherein the metal catalyst is in gaseous phase and the metal catalyst in gaseous phase is in admixture with a carrier gas.
9. The method of any one of claims 1 to 7, wherein the metal catalyst is in liquid phase and the metal catalyst in liquid phase is in admixture with a carrier gas.
10. The method of any one of claims 1 to 6, wherein the metal catalyst is in solid phase and the metal catalyst in solid phase is in admixture with a carrier gas, and wherein the mixture of the metal catalyst in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.

11. The method of claim 1, wherein step (c) is carried out by directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma.

12. The method of claim 11, wherein the carbon-containing
5 substance and the metal catalyst are in liquid or gaseous phase and the carbon-containing substance and metal catalyst in liquid or gaseous phase flow along a helical path prior to contacting the primary plasma.

13. The method of claim 11 or 12, wherein the carbon-containing substance and the metal catalyst are in gaseous phase and the carbon-
10 containing substance and metal catalyst in gaseous phase are in admixture with a carrier gas.

14. The method of claim 11 or 12, wherein the carbon-containing substance and the metal catalyst are in liquid phase and the carbon-
15 containing substance and metal catalyst in liquid phase are in admixture with a carrier gas.

15. The method of claim 11, wherein the carbon-containing substance and the metal catalyst are in solid phase and the carbon-
containing substance and metal catalyst in solid phase are in admixture with
a carrier gas, and wherein the mixture of the carbon-containing substance,
20 the metal catalyst in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.

16. The method of any one of claims 1 to 15, wherein the metal catalyst comprises at least one metal selected from the group consisting of Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Ce, Mn, Li, Pr, Nd, Tb, Dy, Ho, Er, Lu
25 and Gd.

17. The method of claim 16, wherein the metal catalyst comprises iron.
18. The method of any one of claims 1 to 15, wherein said metal catalyst comprises cobalt and at least one metal selected from the group consisting of Ni, Fe, Y, Pt, Mo, Cu, Pb and Bi.
19. The method of any one of claims 1 to 15, wherein said metal catalyst comprises nickel and at least one metal selected from the group consisting of Fe, Y, Lu, Pt, B, Ce, Mg, Cu and Ti.
20. The method of any one of claims 1 to 19, wherein the metal catalyst is an organometallic complex.
21. The method of claim 20, wherein the organometallic complex is selected from the group consisting of ferrocene, iron pentacarbonyl, iron (II) phthalocyanine and mixtures thereof.
22. The method of claim 21, wherein the organometallic complex is ferrocene.
23. The method of any one of claims 1 to 19, wherein the metal catalyst is an inorganic metal complex or an inorganic metal catalyst comprising at least one metal in metallic form.
24. The method of any one of claims 1 to 19, wherein the inert gas is in admixture with an inorganic metal catalyst.
25. A method for producing single-wall carbon nanotubes, comprising the steps of:

- a) providing a plasma torch having a plasma tube with a plasma-discharging end;
- b) feeding an inert gas and an inorganic metal catalyst through said plasma tube to form a primary plasma containing atoms of said metal catalyst;
- 5 c) contacting a carbon-containing substance with said primary plasma at the plasma-discharging end of said plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of said metal catalyst; and
- 10 d) condensing the atoms or molecules of carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.

26. The method of claim 25, wherein step (c) is carried out by directing the carbon-containing substance towards the primary plasma.

27. The method of claim 25 or 26, wherein the carbon-containing substance is in liquid or gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma.

15

28. The method of any one of claims 25 to 27, wherein the carbon-containing substance is in gaseous phase and the carbon-containing substance in gaseous phase is in admixture with a carrier gas.

20

29. The method of any one of claims 25 to 27, wherein the carbon-containing substance is in liquid phase and the carbon-containing substance in liquid phase is in admixture with a carrier gas.

30. The method of claim 25 or 26, wherein the carbon-containing substance is in solid phase and the carbon-containing substance in solid

25

phase is in admixture with a carrier gas, and wherein the mixture of the carbon-containing substance in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.

31. The method of any one of claims 25 to 30, wherein the
5 inorganic metal catalyst comprises at least one metal selected from the group consisting of Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Ce, Mn, Li, Pr, Nd, Tb, Dy, Ho, Er, Lu and Gd.

32. The method of claim 31, wherein the inorganic metal catalyst comprises iron.

10 33. The method of any one of claims 25 to 30, wherein said metal catalyst comprises cobalt and at least one metal selected from the group consisting of Ni, Fe, Y, Pt, Mo, Cu, Pb and Bi.

34. The method of any one of claims 25 to 30, wherein said metal catalyst comprises nickel and at least one metal selected from the group
15 consisting of Fe, Y, Lu, Pt, B, Ce, Mg, Cu and Ti.

35. The method of any one of claims 25 to 34, wherein the inorganic metal catalyst is an inorganic metal complex or an inorganic metal catalyst comprising at least one metal in metallic form.

36. The method of claim 35, wherein the metal in metallic form is
20 iron.

37. The method of any one of claims 1 to 36, wherein the carbon-containing substance is a carbon-containing gas.

38. The method of any one of claims 1 to 36, wherein the carbon-containing substance is a carbon-containing liquid.
39. The method of any one of claims 1 to 36, wherein the carbon-containing substance is a carbon-containing solid.
- 5 40. The method of any one of claims 1 to 36, wherein the carbon-containing substance comprises a mixture of a carbon-containing gas and a carbon-containing liquid.
41. The method of any one of claims 1 to 36, wherein the carbon-containing substance comprises a mixture of a carbon-containing
10 gas and a carbon-containing solid.
42. The method of any one of claims 1 to 36, wherein the carbon-containing substance comprises a mixture of a carbon-containing liquid and a carbon-containing solid.
43. The method of any one of claims 1 to 36, wherein the
15 carbon-containing substance comprises a mixture of a carbon-containing gas, a carbon-containing liquid and a carbon-containing solid.
44. The method of any one of claims 37, 40, 41 and 43, wherein the carbon-containing gas is a C₁-C₄ hydrocarbon.
45. The method of claim 44, wherein the C₁-C₄ hydrocarbon is
20 methane or ethylene.
46. The method of any one of claims 38, 40, 42 and 43, wherein the carbon-containing liquid is selected from the group consisting of

pentane, hexane, cyclohexane, heptane, benzene, toluene, xylene, styrene, and mixtures thereof.

47. The method of claim 39, wherein the carbon-containing solid is graphite in the form of a nano-powder.

5 48. The method of any one of claims 1 to 47, wherein the inert gas is selected from the group consisting of helium, argon, and a mixture thereof.

49. The method of claim 48, wherein the inert gas is argon.

10 50. The method of any one of claims 1 to 49, wherein the inert gas flows along a helical path.

51. The method of any one of claims 1 to 50, wherein a cooling inert gas is injected downstream of the secondary plasma.

52. The method of claim 51, wherein the cooling inert gas is selected from the group consisting of helium, argon and a mixture thereof.

15 53. The method of claim 52, wherein the cooling inert gas is helium.

54. The method of any one of claims 4, 5, 6, 8, 9, 10, 13, 14, 15, 28, 29, and 30, wherein the carrier gas is selected from the group consisting of helium, argon, hydrogen, hydrogen sulfide and mixtures thereof.

20 55. The method of claim 54, wherein the carrier gas is argon.

56. The method of any one of claims 1 to 55, wherein the metal catalyst and the carbon-containing substance are used in an atomic ratio metal atoms / carbon atoms of about 0.01 to about 0.06.

57. The method of claim 56, wherein the atomic ratio metal atoms
5 / carbon atoms is about 0.02.

58. The method of any one of claims 1 to 57, wherein step (d) is carried out to provide a temperature gradient permitting rapid condensation of the atoms or molecules of carbon and the atoms of said metal catalyst.

59. The method of claim 58, wherein said temperature gradient is
10 provided by directing the atoms or molecules of carbon and the atoms of said metal catalyst through an oven disposed downstream of said plasma tube in spaced relation thereto, said oven being heated at a predetermined temperature.

60. The method of claim 59, wherein said predetermined
15 temperature is comprised between 500 and 1800 °C.

61. The method of claim 60, wherein said metal catalyst comprises iron and wherein said predetermined temperature is about 900 °C.

62. The method of any one of claims 1 to 61, wherein a further
20 inert gas is injected in said plasma torch and is directed towards said primary and secondary plasmas.

63. The method of claim 62, wherein said further inert gas is helium.

64. The method of any one of claims 1 to 63, further including the step of collecting said single-wall carbon nanotubes by means of a trap.

65. An apparatus for producing single-wall carbon nanotubes, comprising:

5 a plasma torch having a plasma tube for receiving an inert gas so as to form a primary plasma, said plasma tube having a plasma-discharging end;

feed means for directing a carbon-containing substance and a metal catalyst towards said primary plasma so that the carbon-containing
10 substance and the metal catalyst contact said primary plasma at the plasma-discharging end of said plasma tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of said metal catalyst; and

condensing means for condensing the atoms or molecules of
15 carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.

66. The apparatus of claim 65, wherein said feed means comprise a first conduit for directing said carbon-containing substance towards the primary plasma and a second conduit for directing said metal catalyst
20 towards the primary plasma.

67. The apparatus of claim 66, wherein said first and second conduits each have a discharge end disposed adjacent the plasma-discharging end of said plasma tube.

68. The apparatus of claim 65, wherein said feed means comprise
25 a single conduit for directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma.

69. The apparatus of claim 68, wherein said conduit has a discharge end disposed adjacent to the plasma-discharging end of said plasma tube.

70. The apparatus of claim 69, wherein said conduit is disposed
5 inside said plasma tube and extends substantially coaxially thereof.

71. An apparatus for producing single-wall carbon nanotubes, comprising:

a plasma torch having a plasma tube for receiving an inert gas and an inorganic metal catalyst so as to form a primary plasma containing
10 atoms of said metal catalyst, said plasma tube having a plasma-discharging end;

feed means for directing a carbon-containing substance towards said primary plasma so that the carbon-containing substance contacts said primary plasma at the plasma-discharging end of said plasma
15 tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of said metal catalyst; and

condensing means for condensing the atoms or molecules of carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.

20 72. The apparatus of claim 71, wherein said feed means comprise a single conduit for directing the carbon-containing substance towards the primary plasma.

73. The apparatus of claim 72, wherein said conduit has a discharge end disposed adjacent the plasma-discharging end of said plasma
25 tube.

74. The apparatus of claim 73, wherein said conduit is disposed inside said plasma tube and extends substantially coaxially thereof.

75. The apparatus of claim 70 or 74, further including a heat-resistant tubular member disposed about said plasma tube and extending
5 substantially coaxially thereof, and means for injecting a further inert gas between said plasma tube and said tubular member to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end of said plasma tube.

76. The apparatus of any one of claims 65 to 75, wherein said
10 condensing means comprise an oven disposed downstream of said plasma tube in spaced relation thereto, and a heat source for heating said oven to provide a temperature gradient permitting rapid condensation of the atoms or molecules of carbon and the atoms of said metal catalyst.

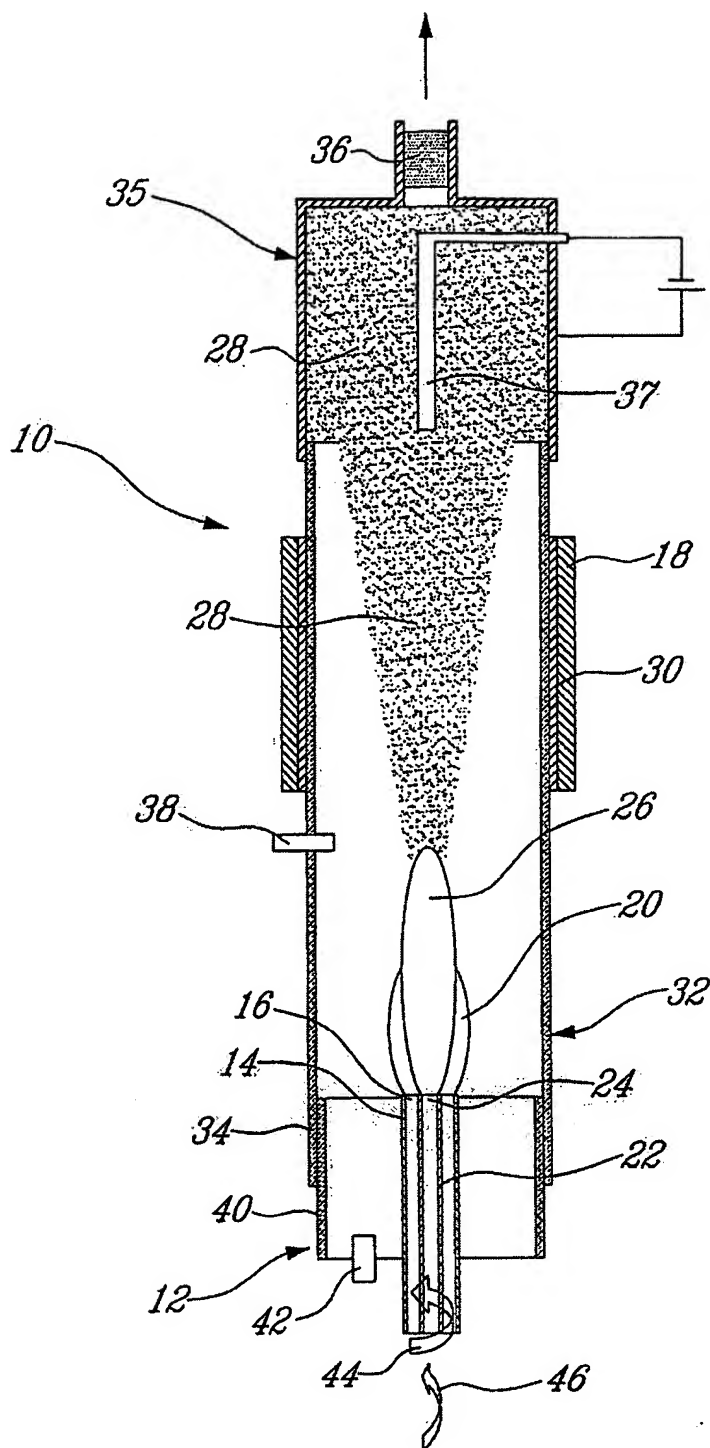
77. The apparatus of claim 76, further including a heat-resistant
15 tubular member extending through said oven and having a plasma-receiving end disposed upstream of the plasma-discharging end of said plasma tube, and injection means for injecting a cooling inert gas into said tubular member and downstream of the secondary plasma, said cooling inert gas assisting in providing the temperature gradient.

20 78. The apparatus of claim 75 or 77, wherein said heat-resistant tubular member is made of quartz or boron nitride.

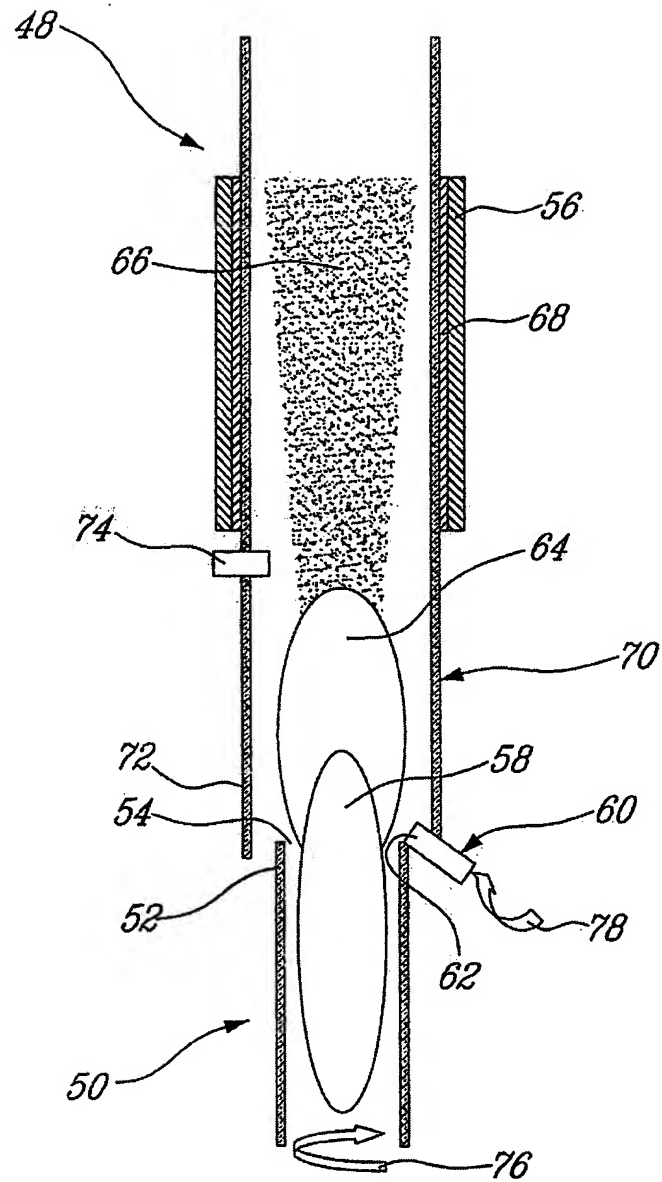
79. The apparatus of any one of claims 65 to 78, further including a trap for collecting said single-wall carbon nanotubes.

80. The apparatus of claim 79, wherein said trap is an electrostatic
25 trap.

1 / 8

FIG. 1

2 / 8

FIG. 2

4/8

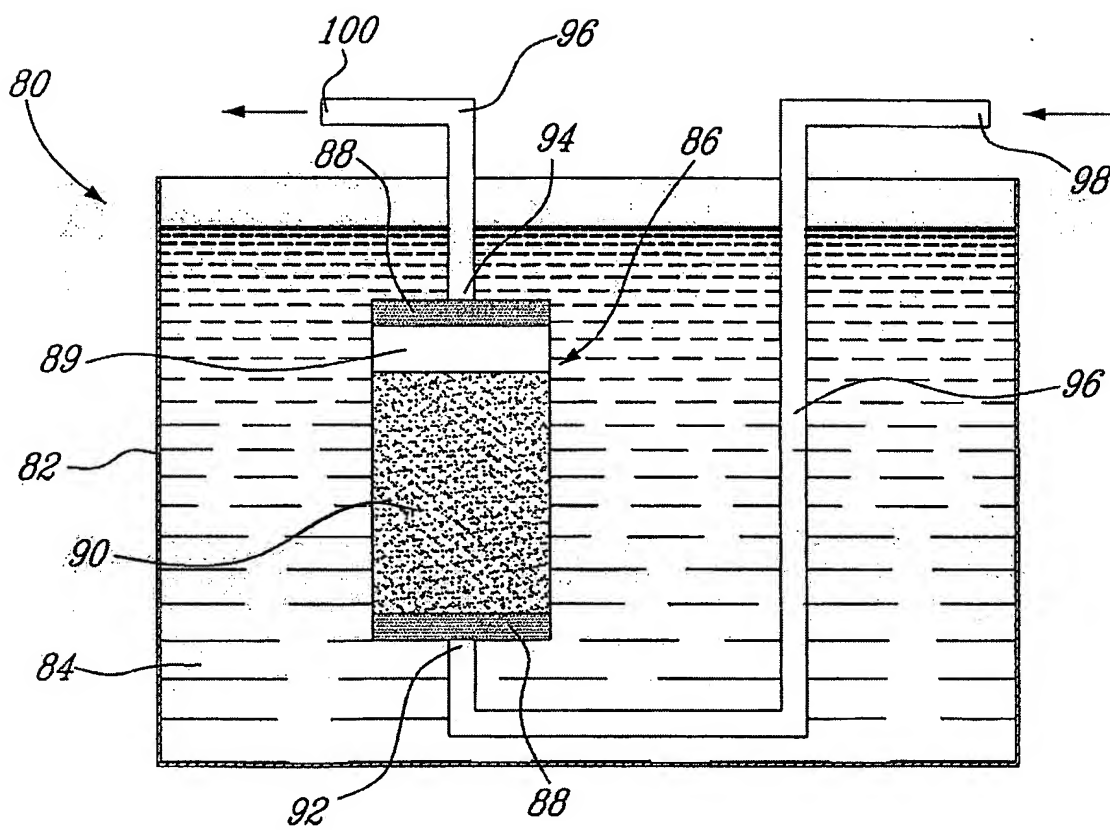


FIG. 4

5/8

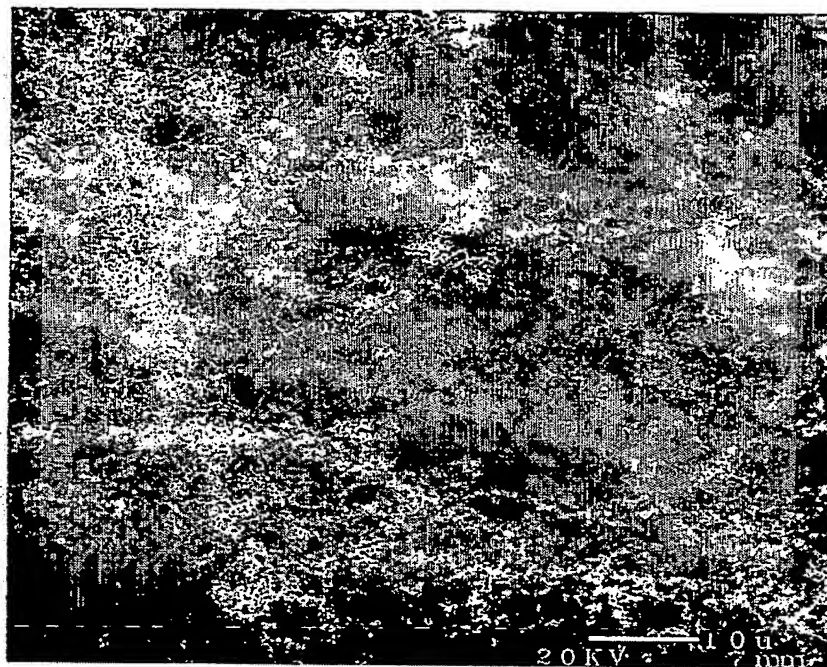


FIG 5

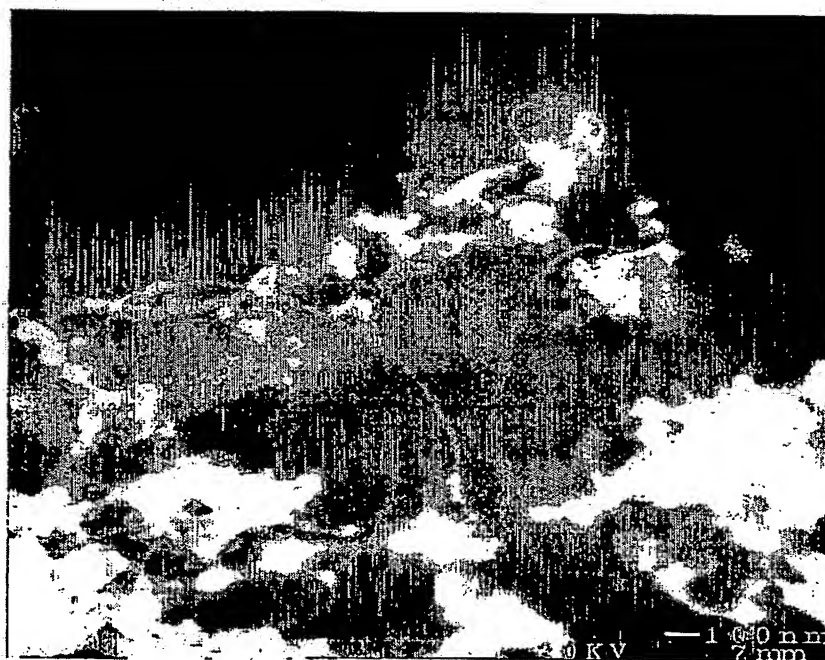


FIG. 6

6/8

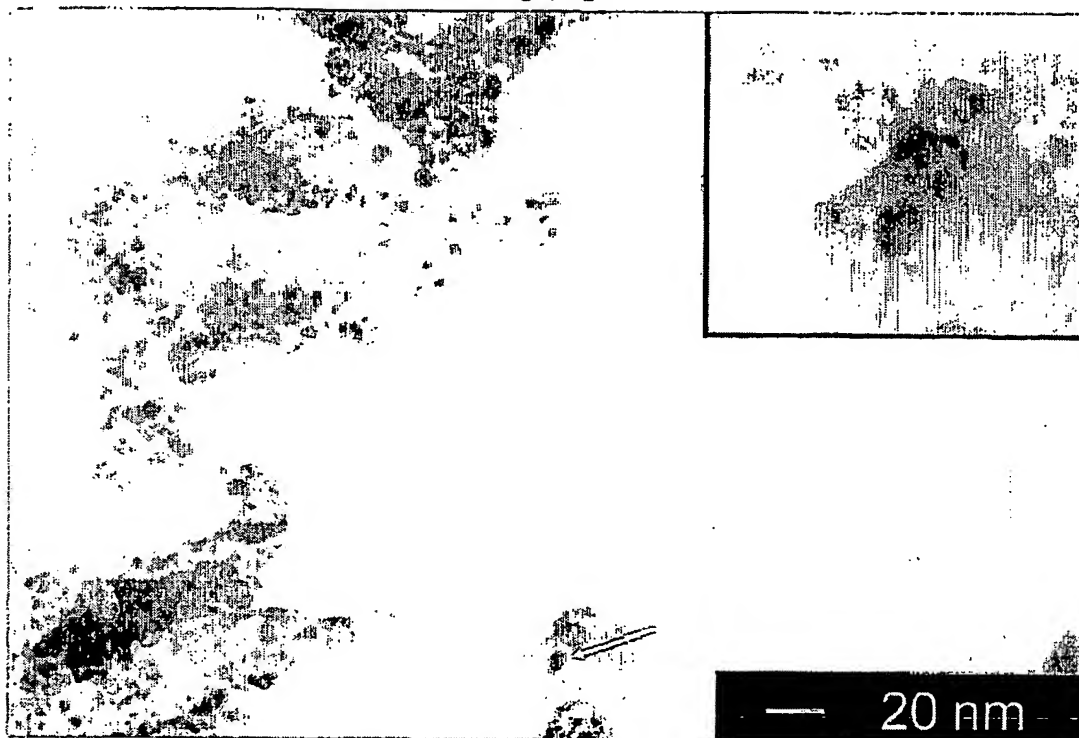


FIG. 7

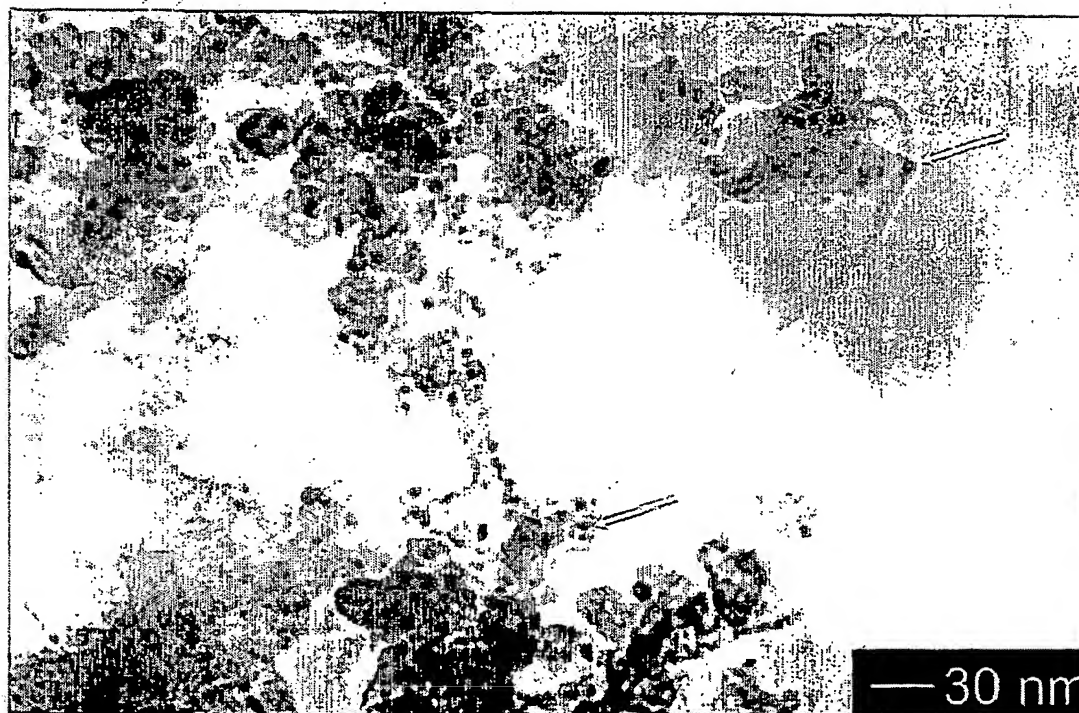
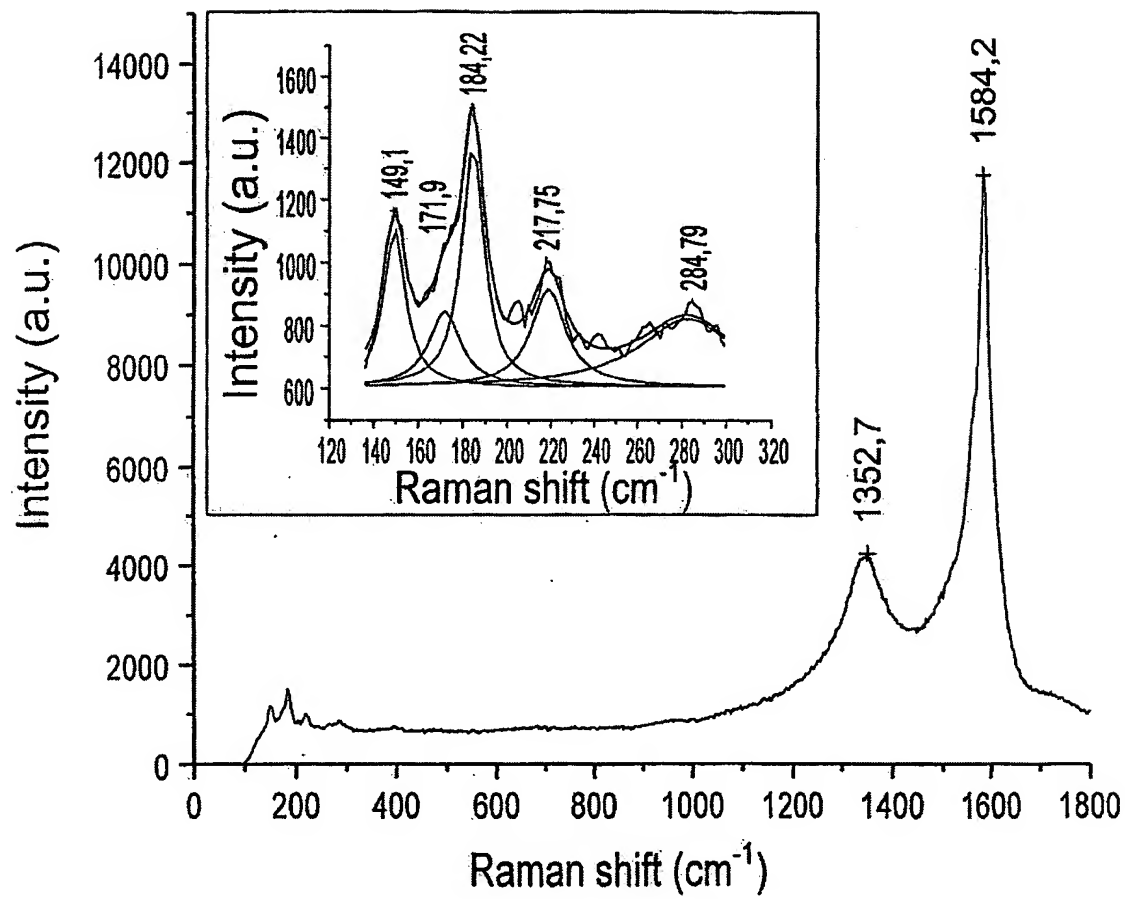
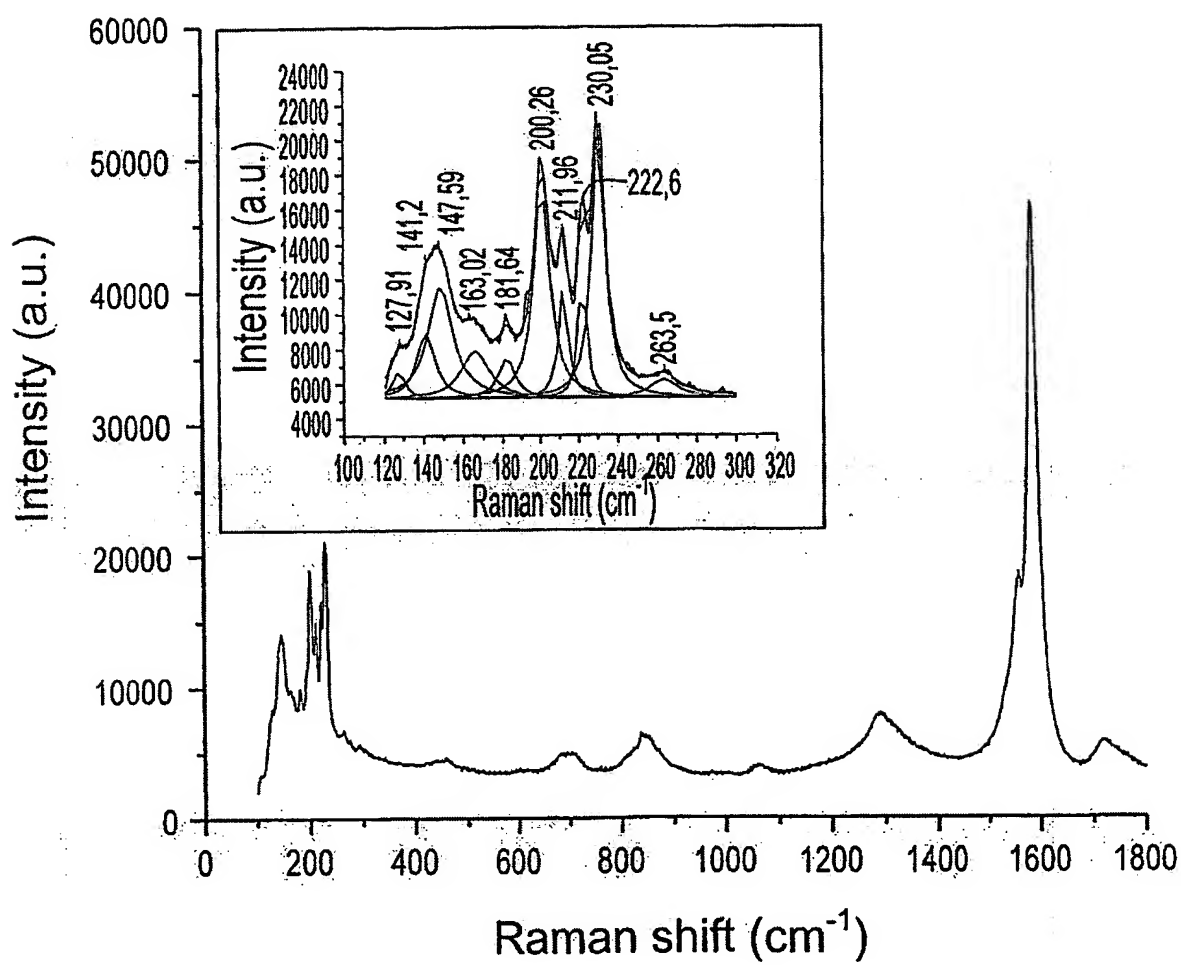


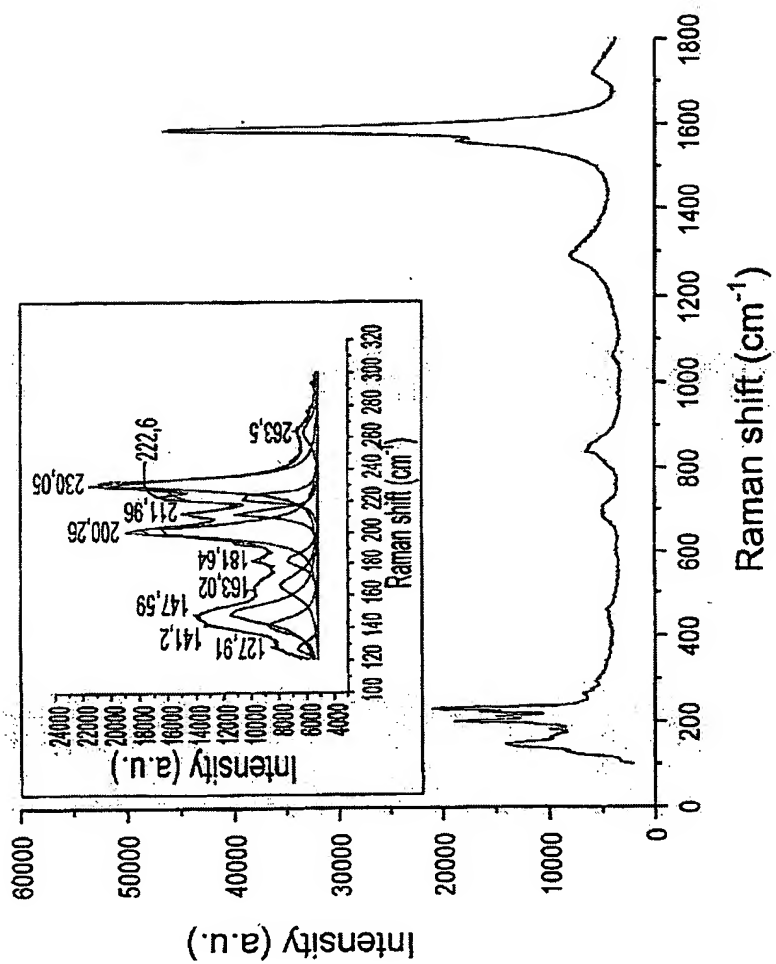
FIG. 8

7 / 8

FIG. 9

8/8

FIG. 10



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.